Recoverable, Reusable, Highly Active, and Sulfur-tolerant Polymer Incarcerated Palladium for Hydrogenation

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SUPPORTING INFORMATION

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General

Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^1H NMR and CDCl_3 ($\delta = 77.0$) for ^{13}C NMR. Reactions under a controlled pressure of hydrogen were performed with a stainless reactor. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

2-[2-(4-Vinylphenyl)ethoxymethyl]oxirane (3): To sodium hydride (60% in mineral oil, 1.92 g, 48 mmol) suspended in tetrahydrofuran (40 mL) was added a solution of 2-(4-vinylphenyl)ethanol¹ (2.37 g, 16 mmol) in tetrahydrofuran (9 mL) at 0 °C. After the mixture was stirred for 1 h at room temperature, 18-crown-6 (422

mg, 1.6 mmol) and epichlorohydrin (4.44 g, 48 mmol) were added, and the mixture was further stirred for 12 h. After the mixture was cooled to 0 °C and diluted with diethyl ether, saturated aqueous ammonium chloride was added to quench the reaction, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt/hexane) to afford 2-[2-(4-vinylphenyl)ethoxymethyl]oxirane (**3**, 2.88 g, 88 %). ¹H NMR (CDCl₃) δ = 2.58 (dd, 1H, *J* = 2.7 Hz, 5.0 Hz), 2.77 (dd, 1H, *J* = 4.1 Hz, 5.0 Hz), 2.89 (t, 2H, *J* = 7.1 Hz), 3.10-3.15 (m, 1H), 3.39 (dd, 1H, *J* = 5.7, 11.5 Hz), 3.64-3.77 (m, 3H), 5.20 (dd, 1H, *J* = 0.9 Hz, 10.8 Hz), 5.70 (dd, 1H, *J* = 0.9 Hz, 17.6 Hz), 6.69 (dd, 1H, *J* = 10.8 Hz, 17.6 Hz), 7.18 (d, 2H, *J* = 8.1 Hz), 7.33 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (CDCl₃) δ = 36.0, 44.2, 50.8, 71.5, 72.2, 113.2, 126.2, 129.0, 135.6, 136.6, 138.4; IR (KBr) 3000, 2924, 2867, 1911, 1812, 1701, 1630, 1512, 1479, 1407, 1337, 1254, 1205, 1107, 991, 909, 839 cm⁻¹; HRMS (EI) Calcd for C₁₃H₁₆O₂ (M⁺) 204.1150, found 204.1130.

Copolymer (1b): Styrene (6.33 g, 60.8 mmol), 2-[2-(4-vinylphenyl)ethoxymethyl]oxirane (**3**, 1.55 g, 7.6 mmol), tetraethyleneglycol mono-2-phenyl-2-propenyl ether² (**4**, 2.36 g, 7.6 mmol), and 2,2'-azobis(isobutyronitrile) (69.9 mg, 0.42 mmol) were mixed in chloroform (10 mL). The mixture was stirred for 48 h under reflux conditions and then cooled to room temperature. The resulting polymer solution was poured slowly into methanol. The precipitated polymer was filtered and washed with methanol several times and dried for 24 h under reduced pressure to afford the desired copolymer (**1b**, 6.72 g, 66% yield). The molar ratio of the components was determined by ¹H-NMR analysis (styrene : **3** : **4** = 88 : 7 : 5). Mw: 41,741, Mn: 25,922, Mw / Mn = 1.61 (GPC).

Preparation of polymer incarcerated palladium (PI Pd (2b)): Copolymer (**1b**, 1.00 g) was dissolved in tetrahydrofuran (20 mL) at room temperature, and to this

solution was added tetrakis(triphenylphosphine)palladium(0) ($\text{Pd(PPh}_3)_4$), 1.0 g) as a core. The mixture was stirred for 24 h at this temperature. Hexane (30 mL) was slowly added to the mixture at 0 °C. Coacervates were found to envelope the core dispersed in the medium. The mixture was left to stand at room temperature for 12 h, and the catalyst capsules were then washed with hexane several times and dried at room temperature for 24 h. Next, the catalyst capsules were stirred at 120 °C for 2 h to cross-link the polymer chain. The cross-linked catalyst was then washed with tetrahydrofuran several times and dried at room temperature for 24 h to give polymer incarcerated palladium (PI Pd **2b**, 1.04 g, 0.707 mmol/g of palladium metal was loaded).

Determination of loading of the palladium: PI Pd (**2b**, 50.0 mg) was placed in 50 mL-test tube, and sulfuric acid (1.0 mL) was added. The mixture was heated at 180 °C for 30 min, and nitric acid (0.5 mL) was added. The mixture was further heated for 1 h to give a clear solution. The solution was diluted with water, and was measured the palladium metal by fluorescence X-ray (XRF) analysis.

A typical experimental procedure for the hydrogenation.

5,6,7,8-Tetrahydro-2-methoxynaphthalene and 1,2,3,4-Tetrahydro-2-methoxynaphthalene (12 and 13): PI Pd (**2b**, 0.025 mmol, 5 mol%) and 2-methoxynaphthalene (79.1 mg, 0.50 mmol) were combined in ethanol (7 mL). The mixture was stirred for 18 h at 50 °C under 70 atm of hydrogen pressure. The catalyst was filtered and washed with tetrahydrofuran, and the solvents of the filtrate were removed under reduced pressure. The residue was purified by PTLC to afford a mixture of 5,6,7,8-tetrahydro-2-methoxynaphthalene (**12**) and 1,2,3,4-tetrahydro-2-methoxynaphthalene (**13**) (81.1 mg, conv. 100 %, **12/13** = 73/27). Recovered PI Pd was dried under reduced pressure and reused.

5,6,7,8-Tetrahydro-2-methoxynaphthalene (12):³ ¹H NMR (CDCl₃) δ = 1.74-1.79 (m, 4H), 2.69-2.73 (m, 4H), 3.79 (s, 3H), 6.60 (d, 1H, J = 2.6 Hz), 6.68 (dd, 1H, J = 2.6 Hz, 8.4 Hz), 6.97 (d, 1H, J = 8.4 Hz).

1,2,3,4-Tetrahydro-2-methoxynaphthalene (13):⁴ ¹H NMR (CDCl₃) δ = 1.74-1.86 (m, 1H), 2.05-2.09 (m, 1H), 2.68-3.10 (m, 4H), 3.42 (s, 3H), 3.62-3.68 (m, 1H), 7.05-7.11 (m, 4H).

Pioglitazone (8):⁵ ¹H NMR (DMSO-d₆) δ = 1.18 (t, 3H, J = 7.5 Hz), 2.58 (q, 2H, J = 7.5 Hz), 3.04 (dd, 1H, J = 9.0 Hz, 14.1 Hz), 3.13 (t, 2H, J = 6.6 Hz), 3.30 (dd, 1H, J = 4.4 Hz, 14.1 Hz), 4.30 (t, 2H, J = 6.6 Hz), 4.85 (dd, 1H, J = 4.4 Hz, 9.0 Hz), 6.86 (d, 2H, J = 8.6 Hz), 7.13 (d, 2H, J = 8.6 Hz), 7.27 (d, 1H, J = 8.1 Hz), 7.56 (dd, 1H, J = 2.2 Hz, 8.1 Hz), 8.36 (s, 1H).

9,10-Dihydrophenanthrene (9):⁶ ¹H NMR (CDCl₃) δ = 2.86 (s, 4H), 7.20-7.31 (m, 6H), 7.72-7.74 (m, 2H).; ¹³C NMR (CDCl₃) δ = 29.0, 123.7 126.9 127.3 128.1 134.5 137.3.

1,2,3,4,5,6,7,8-octahydrophenanthrene (10):⁶ ¹H NMR (CDCl₃) δ = 1.72-1.79 (m, 8H), 2.53 (m, 4H), 2.72 (m, 4H), 6.85 (s, 2H); ¹³C NMR (CDCl₃) δ = 22.8, 23.5, 26.2, 30.0, 126.4, 134.3, 135.2.

1,2,3,4,4a,9,10,10a-octahydrophenanthrene (11):⁷ ¹H NMR (CDCl₃) δ = 0.90-3.09 (m, 14H), 7.0-7.30 (m, 4H).

2,4-Diphenyl-2-methylpentane:⁸ ¹H NMR (CDCl₃) δ = 1.02 (d, 3H, J = 6.8 Hz), 1.14 (s, 3H), 1.24 (s, 3H), 1.94 (dd, 1H, J = 5.0 Hz, 14.0 Hz), 2.05 (dd, 1H, J = 7.2 Hz, 14.0 Hz), 2.53 (m, 1H), 7.00-7.29 (m, 10H); ¹³C NMR (CDCl₃) δ = 25.1, 28.2, 31.0, 37.0, 38.4, 52.7, 125.4, 125.5, 126.0, 127.0, 127.9, 128.2, 149.2, 149.3.

1,2-Dimethoxy-4-propylbenzene⁹: ¹H NMR (CDCl₃) δ = 0.94 (t, 3H, *J* = 7.3 Hz), 1.57-1.67 (m, 2H), 2.53 (t, 2H, *J* = 7.3 Hz), 3.84 (s, 3H), 3.86 (s, 3H), 6.70-6.79 (m, 3H); ¹³C NMR (CDCl₃) δ = 13.7, 24.6, 37.5, 55.6, 55.7, 111.0, 111.7, 120.1, 135.2, 146.9, 148.6.

3-Phenylpropanol: ¹H NMR (CDCl₃) δ = 1.82-1.91 (m, 2H), 2.10 (s, 1H), 2.68 (t, 2H, *J* = 7.7 Hz), 3.63 (t, 2H, *J* = 6.4 Hz), 7.15-7.29 (m, 5H); ¹³C NMR (CDCl₃) δ = 32.0, 34.1, 62.2, 125.8, 128.3, 128.4, 141.8.

Phenyl β-D-glucopyranoside: ¹H NMR (DMSO-d₆) δ = 3.10-3.38 (m, 4H), 3.41-3.49 (m, 1H), 3.68 (ddd, 1H, *J* = 1.8 Hz, 5.3 Hz, 11.7 Hz), 4.54 (t, 1H, 5.7 Hz), 4.84 (d, 1H, *J* = 7.3 Hz), 5.00 (d, 1H, *J* = 5.1 Hz), 5.06 (d, 1H, *J* = 4.4 Hz), 5.28 (d, 1H, *J* = 4.8 Hz), 6.95-7.03 (m, 3H), 7.25-7.31 (m, 2H); ¹³C NMR (DMSO-d₆) δ = 60.7, 69.7, 73.2, 76.6, 77.0, 100.4, 116.2, 121.7, 129.4, 157.5.

1,2,3,4-Tetrahydroquinoline¹⁰: ¹H NMR (CDCl₃) δ = 1.87-1.95 (m, 2H), 2.76 (t, 2H, *J* = 6.4 Hz), 3.24-3.28 (m, 2H), 3.70 (brs, 1H), 6.44 (d, 1H, *J* = 7.7 Hz), 6.58 (t, 1H, *J* = 7.5 Hz), 6.91-6.97 (m, 2H, *J* = 7.7 Hz); ¹³C NMR (CDCl₃) δ = 22.2, 27.0, 41.9, 114.1, 116.8, 121.3, 126.7, 129.4, 144.8.

2,3-Dihydrobenzo[*b*]thiophene¹¹: ¹H NMR (CDCl₃) δ = 3.24-3.34 (m, 4H), 6.99 (t, 1H, *J* = 7.2 Hz), 7.09 (t, 1H, *J* = 7.2 Hz), 7.15-7.22 (m, 2H).

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